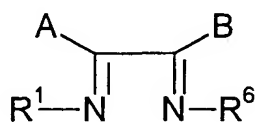


CLAIMS

We claim:

1. A catalyst for the polymerization of olefins comprising a complex comprising (a) a ligand of the formula **X**, (b) a group 8-10 transition metal, and optionally (c) a Bronsted or Lewis acid,



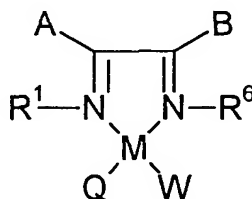
**X**

$\text{R}^1$  and  $\text{R}^6$  are each, independently, hydrocarbyl, substituted hydrocarbyl, or silyl; N represents nitrogen; and

- 10 A and B are each, independently, a heteroatom connected mono-radical wherein the connected heteroatom is selected from Group 15 or 16; in addition, A and B may be linked by a bridging group; wherein the complex is attached to a solid support, and wherein the solid support, the optional Bronsted or Lewis acid, and the complex are combined in any
- 15 order to form said catalyst.

2. The catalyst of claim 1 wherein the solid support is pretreated with a Bronsted or Lewis acid.

3. A catalyst for the polymerization of olefins comprising the reaction product of a compound of formula **XII**, a compound Y and a solid support:
- 20



**XII**

$R^1$  and  $R^6$  each, independently, represent hydrocarbyl, substituted hydrocarbyl, or silyl;

A and B are each, independently, a heteroatom connected mono-radical wherein the connected heteroatom is selected from Group 15 or 16;

5 in addition, A and B may be linked by a bridging group;

Q represents an alkyl, chloride, iodide or bromide;

W represents an alkyl, chloride, iodide or bromide;

N represents nitrogen; and

M represents Ni(II), Pd(II), Co(II), or Fe(II);

10 and Y is selected from the group consisting of a neutral Lewis acid

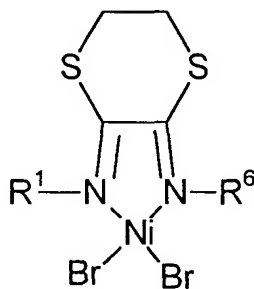
capable of abstracting  $Q^-$  or  $W^-$  to form a weakly coordinating anion, a

cationic Lewis acid whose counterion is a weakly coordinating anion, and a

Bronsted acid whose conjugate base is a weakly coordinating anion.

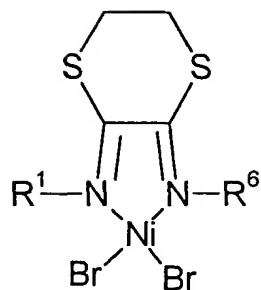
4. The catalyst of claim 3 wherein M is Ni(II).

15 5. The catalyst of claim 3, wherein the compound of formula **XII** is selected from the group consisting of



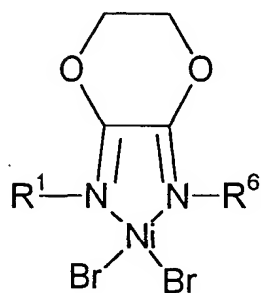
**XXVII**

wherein  $R^1$  and  $R^6$  are 2,6-dimethylphenyl;



**XXVIII**

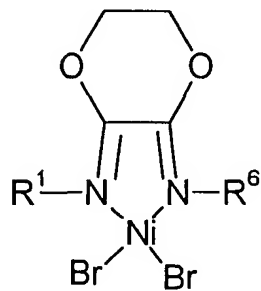
wherein R<sup>1</sup> and R<sup>6</sup> are 2,6-diisopropylphenyl;



**XXXII**

5

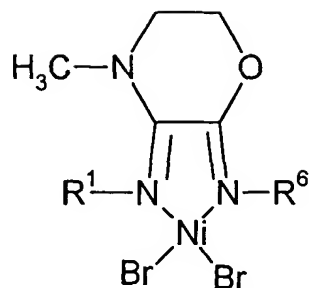
wherein R<sup>1</sup> and R<sup>6</sup> are 2,6-dimethylphenyl;



**XXXIII**

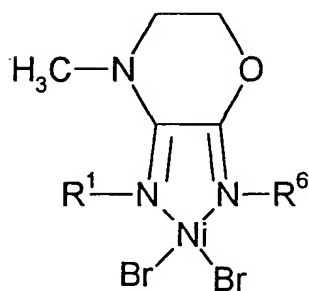
wherein R<sup>1</sup> and R<sup>6</sup> are 2,6-diisopropylphenyl;

10



XXXVIII

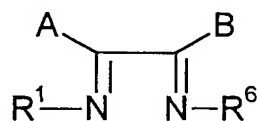
wherein R<sup>1</sup> and R<sup>6</sup> are 2,6-dimethylphenyl; and



XXXIX

5                    wherein R<sup>1</sup> and R<sup>6</sup> are 2,6-diisopropylphenyl.

6.            A process for the preparation of supported catalysts comprising contacting a group 8-10 transition metal complex of a ligand of the formula X, a solid support, and optionally a Bronsted or Lewis acid,



X

10

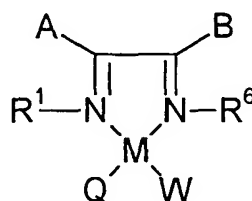
wherein R<sup>1</sup> and R<sup>6</sup> are each, independently, hydrocarbyl, substituted hydrocarbyl, or silyl; N represents nitrogen; and

A and B are each, independently, a heteroatom connected mono-radical wherein the connected heteroatom is selected from Group 15 or 16;

in addition, A and B may be linked by a bridging group; wherein the complex is attached to a solid support, and wherein the solid support, the optional Bronsted or Lewis acid, and the complex are combined in any order to form said supported catalyst.

5           7.     The process of claim 6 wherein the solid support is pretreated with a Bronsted or Lewis acid.

8.     A process for the preparation of supported catalysts comprising contacting a compound of formula XII, a compound Y and a solid support:



XII

10

R<sup>1</sup> and R<sup>6</sup> each, independently, represent hydrocarbyl, substituted hydrocarbyl, or silyl;

A and B are each, independently, a heteroatom connected mono-radical wherein the connected heteroatom is selected from Group 15 or 16; in addition, A and B may be linked by a bridging group;

Q represents an alkyl, chloride, iodide or bromide;

W represents an alkyl, chloride, iodide or bromide;

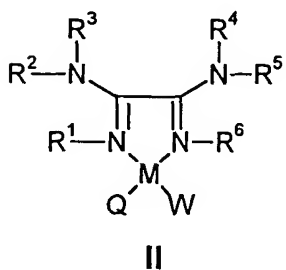
N represents nitrogen; and

20           M represents Ni(II), Pd(II), Co(II), or Fe(II);

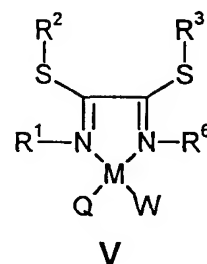
and Y is selected from the group consisting of a neutral Lewis acid capable of abstracting Q<sup>-</sup> or W<sup>-</sup> to form a weakly coordinating anion, a cationic Lewis acid whose counterion is a weakly coordinating anion, and a Bronsted acid whose conjugate base is a weakly coordinating anion.

25           9.     The process of claim 8 wherein M is Ni(II).

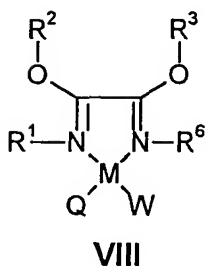
10. The process of claim 8 wherein the compound of formula XII is selected from:



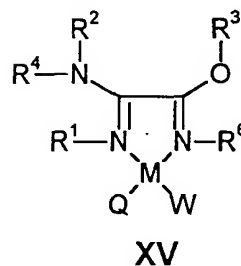
or



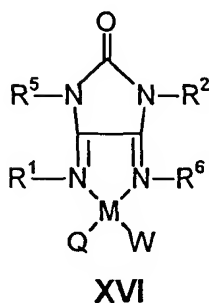
or



or



or



- 5            wherein R<sup>1</sup> and R<sup>6</sup> each, independently, represent hydrocarbyl, substituted hydrocarbyl, or silyl;
- R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup> and R<sup>5</sup> each, independently, represent a hydrogen, hydrocarbyl, substituted hydrocarbyl, or silyl; in addition, any two of R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, and R<sup>5</sup> may collectively form a bridging group, provided that when the
- 10        catalyst is of formula **V** or **VIII**, the bridging group is not a substituted sulfur atom or a substituted phosphorous atom;
- Q represents a hydrocarbyl, chloride, iodide or bromide;
- W represents a hydrocarbyl, chloride, iodide or bromide;

M represents Ni(II), Pd(II), Co(II), or Fe(II); and

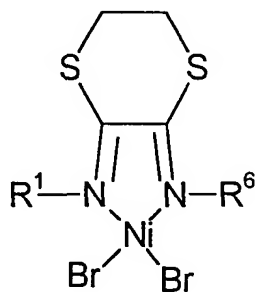
N represents nitrogen.

11. The process of claim 10, wherein the solid support is silica.

12. The process of claim 11, wherein compound Y is selected  
5 from the group consisting of MAO, diethyl aluminum chloride, and trimethyl  
aluminum.

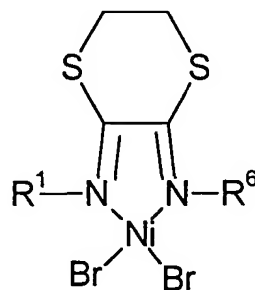
13. The process of claim 12, wherein the compound of formula **XII** is  
selected from **V**, **VIII** and **XV**.

14. The process of claim 8, wherein the compound of formula **XII**  
10 is selected from the group consisting of



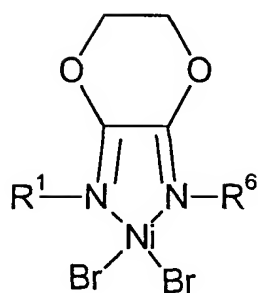
**XXVII**

wherein R¹ and R⁶ are 2,6-dimethylphenyl;



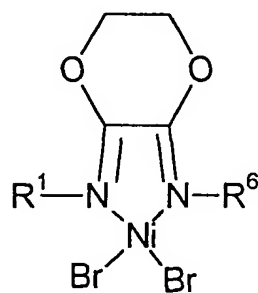
**XXVIII**

wherein R¹ and R⁶ are 2,6-diisopropylphenyl;



XXXII

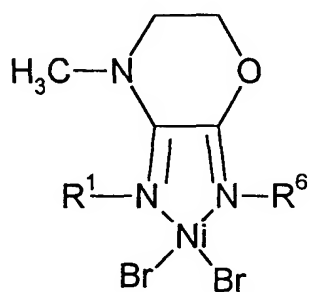
wherein R<sup>1</sup> and R<sup>6</sup> are 2,6-dimethylphenyl;



XXXIII

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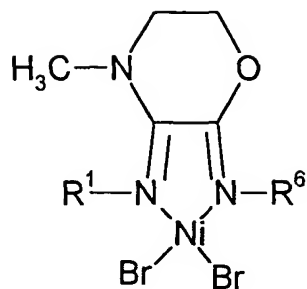
wherein R<sup>1</sup> and R<sup>6</sup> are 2,6-diisopropylphenyl;



XXXVIII

wherein R<sup>1</sup> and R<sup>6</sup> are 2,6-dimethylphenyl; and

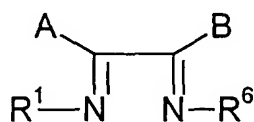




XXXIX

wherein R<sup>1</sup> and R<sup>6</sup> are 2,6-diisopropylphenyl.

15. A process for the polymerization of olefins, comprising contacting one or more monomers of the formula RCH=CHR<sup>8</sup> with a catalyst comprising a group 8-10 transition metal complex of a ligand of the formula X and optionally a Bronsted or Lewis acid,



X

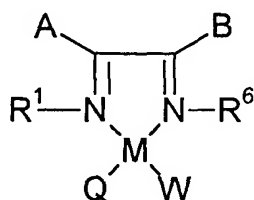
wherein R and R<sup>8</sup> each, independently, represent a hydrogen, a hydrocarbyl, or a fluoroalkyl, and may be linked to form a cyclic olefin;

R<sup>1</sup> and R<sup>6</sup> are each, independently, hydrocarbyl, substituted hydrocarbyl, or silyl; N represents nitrogen; and

A and B are each, independently, a heteroatom connected mono-radical wherein the connected heteroatom is selected from Group 15 or 16; in addition, A and B may be linked by a bridging group; wherein the complex is attached to a solid support, and wherein the solid support, the optional Bronsted or Lewis acid, and the complex are combined in any order.

16. The process of claim 15 wherein the solid support is pretreated with a Bronsted or Lewis acid.

17. A process for the polymerization of olefins, comprising contacting one or more monomers of the formula  $\text{RCH=CHR}^8$  with the reaction product of a compound of formula **XII**, a compound Y and a solid support:



**XII**

5

wherein R and  $\text{R}^8$  each, independently, represent a hydrogen, a hydrocarbyl, or a fluoroalkyl, and may be linked to form a cyclic olefin;  
 $\text{R}^1$  and  $\text{R}^6$  each, independently, represent hydrocarbyl, substituted hydrocarbyl, or silyl;

10

A and B are each, independently, a heteroatom connected mono-radical wherein the connected heteroatom is selected from Group 15 or 16; in addition, A and B may be linked by a bridging group;

Q represents an alkyl, chloride, iodide or bromide;

W represents an alkyl, chloride, iodide or bromide;

15

N represents nitrogen; and

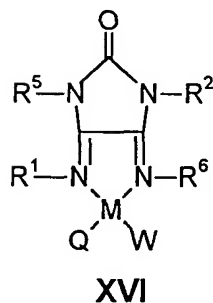
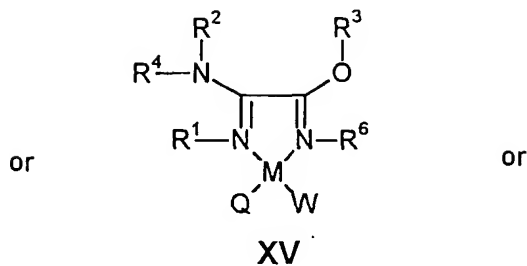
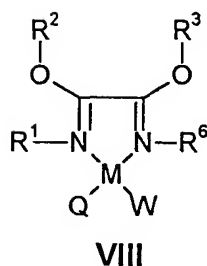
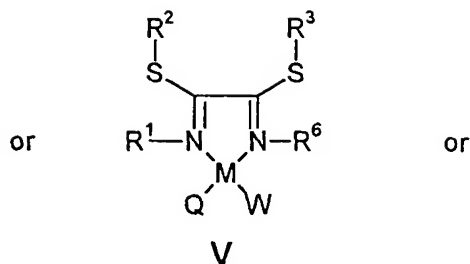
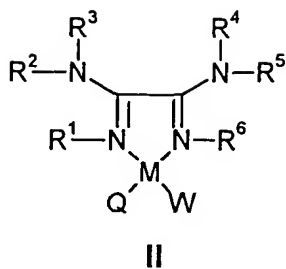
M represents Ni(II), Pd(II), Co(II), or Fe(II);

and Y is selected from the group consisting of a neutral Lewis acid capable of abstracting  $\text{Q}^-$  or  $\text{W}^-$  to form a weakly coordinating anion, a cationic Lewis acid whose counterion is a weakly coordinating anion, and a Bronsted acid whose conjugate base is a weakly coordinating anion.

20

18. The process of claim 17 wherein M is Ni(II).

19. The process of Claim 17 wherein the compound of formula **XII** is selected from:



wherein R and R<sup>8</sup> each, independently, represent hydrogen, hydrocarbyl, or fluoroalkyl, and may be linked to form a cyclic olefin;

R<sup>1</sup> and R<sup>6</sup> each, independently, represent hydrocarbyl, substituted hydrocarbyl, or silyl;

R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup> and R<sup>5</sup> each, independently, represent a hydrogen, hydrocarbyl, substituted hydrocarbyl, or silyl; in addition, any two of R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, and R<sup>5</sup> may collectively form a bridging group, provided that when the catalyst is of formula **V** or **VIII**, the bridging group is not a substituted sulfur atom or a substituted phosphorous atom;

Q represents a hydrocarbyl, chloride, iodide or bromide;

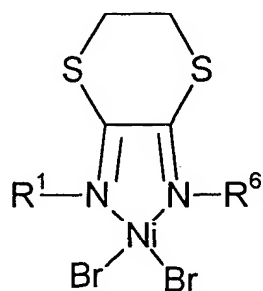
W represents a hydrocarbyl, chloride, iodide or bromide;

M represents Ni(II), Pd(II), Co(II), or Fe(II); and

N represents nitrogen.

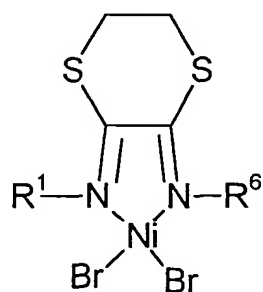
20. The process of claim 19, wherein the compound of formula **XII** is selected from **V**, **VIII** and **XV**.

21. The process of claim 17, wherein the compound of formula **XII**  
5 is selected from the group consisting of



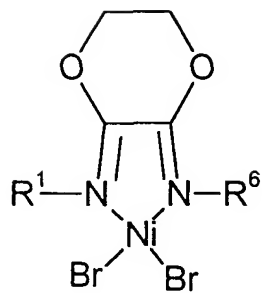
**XXVII**

wherein R<sup>1</sup> and R<sup>6</sup> are 2,6-dimethylphenyl;



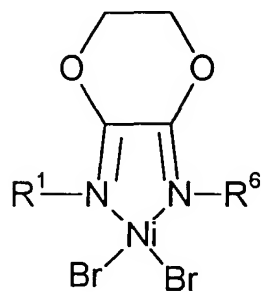
**XXVIII**

wherein R<sup>1</sup> and R<sup>6</sup> are 2,6-diisopropylphenyl;



**XXXII**

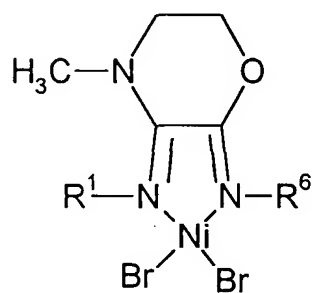
wherein R<sup>1</sup> and R<sup>6</sup> are 2,6-dimethylphenyl;



**XXXIII**

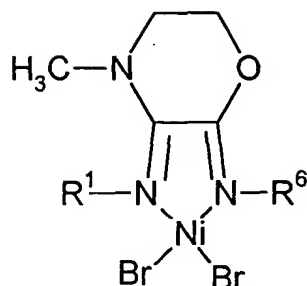
5

wherein R<sup>1</sup> and R<sup>6</sup> are 2,6-diisopropylphenyl;



**XXXVIII**

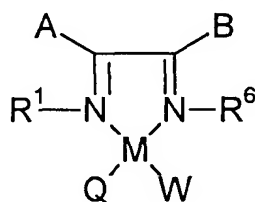
wherein R<sup>1</sup> and R<sup>6</sup> are 2,6-dimethylphenyl; and



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wherein  $R^1$  and  $R^6$  are 2,6-diisopropylphenyl.

22. A process for the polymerization of olefins, comprising  
5 contacting one or more monomers of the formula  $RCH=CHR^8$  with a  
supported catalyst formed by combining a compound of formula XII:



XII

- with a solid support which has been pre-treated with a compound Y,  
wherein R and  $R^8$  each, independently, represent a hydrogen, a  
10 hydrocarbyl, or a fluoroalkyl, and may be linked to form a cyclic olefin;

$R^1$  and  $R^6$  each, independently, represent hydrocarbyl, substituted  
hydrocarbyl, or silyl;

- A and B are each, independently, a heteroatom connected mono-  
radical wherein the connected heteroatom is selected from Group 15 or 16;  
15 in addition, A and B may be linked by a bridging group;

Q represents an alkyl, chloride, iodide or bromide;

W represents an alkyl, chloride, iodide or bromide;

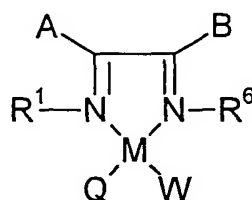
N represents nitrogen; and

M represents Ni(II), Pd(II), Co(II), or Fe(II);

and Y is selected from the group consisting of a neutral Lewis acid capable of abstracting  $Q^-$  or  $W^-$  to form a weakly coordinating anion, a cationic Lewis acid whose counterion is a weakly coordinating anion, and a Bronsted acid whose conjugate base is a weakly coordinating anion.

- 5            23.    A process for the copolymerization of ethylene and a comonomer of the formula  $CH_2=CH(CH_2)_nCO_2R^1$  which comprises contacting ethylene and a comonomer of the formula  $CH_2=CH(CH_2)_nCO_2R^1$  with a supported catalyst formed by combining silica with a compound of the formula **XII** and optionally a compound Y;

10



**XII**

wherein  $R^1$  is hydrogen, hydrocarbyl, substituted hydrocarbyl, fluoroalkyl or silyl;

- 15            n is an integer greater than 3;

$R^1$  and  $R^6$  each, independently, represent hydrocarbyl, substituted hydrocarbyl, or silyl;

A and B are each, independently, a heteroatom connected mono-radical wherein the connected heteroatom is selected from Group 15 or 16;

- 20            in addition, A and B may be linked by a bridging group;

Q represents an alkyl, chloride, iodide or bromide;

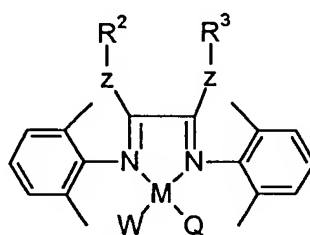
W represents an alkyl, chloride, iodide or bromide;

N represents nitrogen; and

M represents Ni(II), Pd(II), Co(II), or Fe(II);

and Y is selected from the group consisting of a neutral Lewis acid capable of abstracting  $Q^-$  or  $W^-$  to form a weakly coordinating anion, a cationic Lewis acid whose counterion is a weakly coordinating anion, and a Bronsted acid whose conjugate base is a weakly coordinating anion.

- 5            24.    The process described in claim 23 wherein the compound of formula **XXIV** is represented by formula **XXIV**.



**XXIV**

- 10            wherein R<sup>2</sup> and R<sup>3</sup> are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or silyl, or may collectively form a bridging hydrocarbyl, bridging substituted hydrocarbyl, or a substituted silicon atom;  
              Q is alkyl, chloride, iodide or bromide;  
              W is alkyl, chloride, iodide or bromide;  
15            N is nitrogen;  
              Z is sulfur or oxygen; and  
              M is Ni(II).

- 20            25.    A polyethylene composition comprising a blend of polyethylene polymers, wherein said blend has an average degree of branching of from 5 to 120 alkyl branches per 1000 carbon atoms, wherein any individual component of said blend has a degree of branching of from 0 to 150 alkyl branches per 1000 carbon atoms, wherein said polymers are prepared in one reaction vessel, solely from ethylene, and wherein said  
25            polymers are prepared utilizing a Group 8-10 transition metal catalyst which



has been reacted with a solid support and optionally a compound Y, in any order, wherein Y is selected from the group consisting of methylaluminoxane and other aluminum sesquioxides having the formulas  $R^7_3Al$ ,  $R^7_2AlCl$ , and  $R^7AlCl_2$ , wherein  $R^7$  is alkyl.

5           26. The composition of claim 25, wherein the transition metal catalyst is a Ni catalyst.

          27. The composition of claim 26, wherein the compound Y is methylaluminoxane.

          28. A Group 8-10 transition metal catalyst having an improved  
10 rate for the co-polymerization of one or more olefin monomers of the type  $RCH=CHR^8$  with one or more functional olefin monomers of the formula  $CH_2=CH(CH_2)_nJ$ , in an olefin polymerization reaction which comprises combining said catalyst with a solid support, and optionally a Bronsted or Lewis acid in any order, prior to the utilization of said catalyst in said olefin  
15 polymerization reaction.

          wherein R and  $R^8$  each, independently, represent a hydrogen, a hydrocarbyl, or a fluoroalkyl, and may be linked to form a cyclic olefin;

          n is an interger between 1-20;

          J is a group selected from ester, acyl, acid halide, aldehyde, alkyl  
20 amide, aryl, alkylamine, aryl amine, alkyl amido, aryl amido, alkyl imido, aryl imido, ether, nitrile, alcohol, keto, amino, amido, imido, alkoxy thiol, thioalkoxy, acid, urea, sulfonamido, and sulfoester.

          29. The method as described in claim 28 wherein the catalyst is the catalyst of claim 1.

25           30. A ethylene homopolymer with a CDBI of less than 50 %.

          31. The ethylene homopolymer of claim 30 wherein the CDBI is less than 40%.

          32. The ethylene homopolymer of claim 30 wherein the CDBI is less than 30%.

33. A polyalkene with a CDBI of less than 50%, which contains about 80 to about 150 branches per 1000 methylene groups, and which contains for every 100 branches that are methyl, about 30 to about 90 ethyl branches, about 4 to about 20 propyl branches, about 15 to about 50 butyl branches, about 3 to about 15 amyl branches, and about 30 to about 140 hexyl or longer branches.

34. The polyalkene of claim 33 with a CDBI of less than 40%.

35. The polyalkene of claim 33 with a CDBI of less than 30%.

36. The polyalkene as recited in claim 35 which contains about 100 to about 130 branches per 1000 methylene groups, and which contains for every 100 branches that are methyl, about 50 to about 75 ethyl branches, about 5 to about 15 propyl branches, about 24 to about 40 butyl branches, about 5 to about 10 amyl branches, and about 65 to about 120 hexyl or longer branches.

37. The polyalkene of claim 36 with a CDBI of less than 40%.

38. The polyalkene of claim 36 with a CDBI of less than 30%.

39. The polyalkene as recited in claim 33 which is an ethylene homopolymer.

40. A polyalkene with a CDBI of less than 50% which contains about 20 to about 150 branches per 1000 methylene groups, and which contains for every 100 branches that are methyl, about 4 to about 20 ethyl branches, 1 to about 12 propyl branches, 1 to about 12 butyl branches, 1 to about 10 amyl branches, and 0 to about 20 hexyl or longer branches.

41. The polyalkene of claim 40 with a CDBI of less than 40%.

42. The polyalkene of claim 40 with a CDBI of less than 30%.

43. The polyalkene as recited in claim 40 which contains about 40 to about 100 branches per 1000 methylene groups, and which contains for every 100 branches that are methyl, about 6 to about 15 ethyl branches, about 2 to about 10 propyl branches, about 2 to about 10 butyl branches,

about 2 to about 8 amyl branches, and about 2 to about 15 hexyl or longer branches.

44. The polyalkene of claim 43 with a CDBI of less than 40%.

45. The polyalkene of claim 43 with a CDBI of less than 30%.

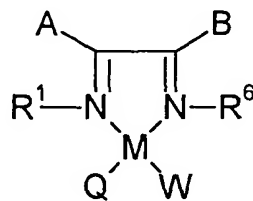
5 46. The polyalkene as recited in claim 40 which is an ethylene homopolymer.

47. A process for the copolymerization of one or more olefin monomers of the type  $RCH=CHR^8$  with one or more functional olefin monomers of the formula  $CH_2=CH(CH_2)_nJ$  comprising a catalyst, in an olefin polymerization reaction which comprises combining a complex of the formula XII, a solid support, and optionally a compound Y, prior to the utilization of said catalyst in said olefin polymerization reaction.

10 wherein R and  $R^8$  each, independently, represent a hydrogen, a hydrocarbyl, or a fluoroalkyl, and may be linked to form a cyclic olefin;  
15 n is an interger between 1-20;

J is a group selected from ester, acyl, acid halide, aldehyde, alkyl amide, aryl, alkylamine, aryl amine, alkyl amido, aryl amido, alkyl imido, aryl imido, ether, nitrile, alcohol, keto, amino, amido, imido, alkoxy thiol, thioalkoxy, acid, urea, sulfonamido, and sulfoester;

20



XII

$R^1$  and  $R^6$  each, independently, represent hydrocarbyl, substituted hydrocarbyl, or silyl;

A and B are each, independently, a heteroatom connected mono-radical wherein the connected heteroatom is selected from Group 15 or 16; in addition, A and B may be linked by a bridging group;

Q represents an alkyl, chloride, iodide or bromide;

5 W represents an alkyl, chloride, iodide or bromide;

N represents nitrogen; and

M represents Ni(II), Pd(II), Co(II), or Fe(II);

and Y is selected from the group consisting of a neutral Lewis acid

capable of abstracting  $Q^-$  or  $W^-$  to form a weakly coordinating anion, a

10 cationic Lewis acid whose counterion is a weakly coordinating anion, and a Bronsted acid whose conjugate base is a weakly coordinating anion.

15